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STRUCTURAL ADHESION (U) VIRGINIA TECH CENTER FOR  
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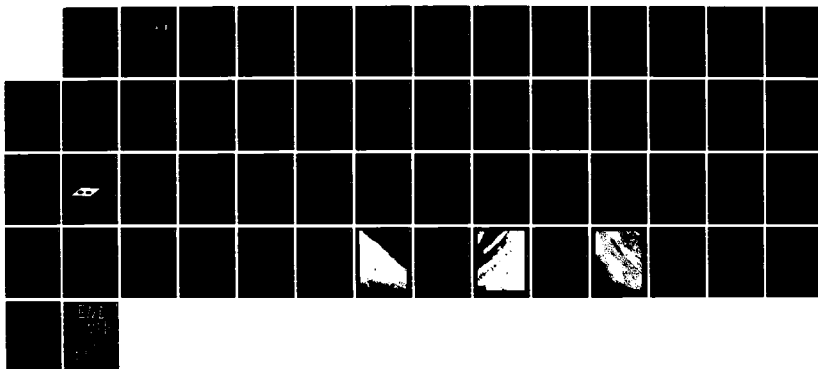
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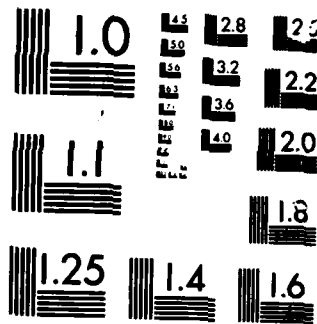
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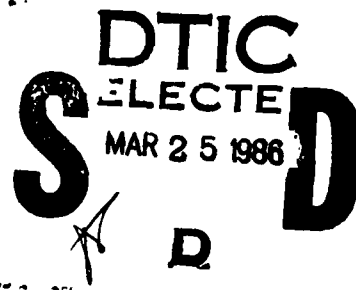


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# VIRGINIA TECH CENTER FOR ADHESION SCIENCE

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ANNUAL REPORT

AN INTERDISCIPLINARY APPROACH TO PREDICTIVE  
MODELING OF STRUCTURAL ADHESIVE BONDING

CHARACTERIZATION OF CHROMIC ACID ANODIZED  
TI-6AL-4V AND ANODIZED TI-6AL-4V SINGLE LAP BONDS  
TO POLYPHENYLQUINOXALINE

BY

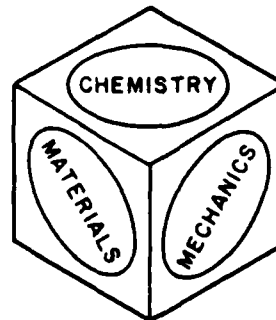
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## TABLE OF CONTENTS

	Page
ACKNOWLEDGEMENTS . . . . .	ii
LIST OF TABLES . . . . .	iv
LIST OF FIGURES . . . . .	v
Chapter	
I. INTRODUCTION . . . . .	1
II. EXPERIMENTAL . . . . .	3
A. Polyphenylquinoxaline - Chromic Acid Anodized Single Lap Bonds . . . . .	3
B. Transmission Electron Microscopy (TEM) and Selected Area Electron Diffraction (SAED) Analyses . . . . .	18
C. CAA Ti-6Al-4V Oxide Electrical Properties .	18
III. RESULTS AND DISCUSSION . . . . .	24
A. PPQ - CAA Ti-6Al-4V Unaged Single Lap Bond Strength . . . . .	24
B. PPQ - CAA Ti-6Al-4V Single Lap Bond Strength After Thermal Aging . . . . .	28
C. Electrical Properties of Anodic Oxide Produced by CAA Without HF . . . . .	29
D. Electrical Properties of Anodic Oxide Produced by CAA With HF . . . . .	33
E. Morphology and Structure of Oxide Produced on Ti-6Al-4V by CAA With HF . . . . .	39
F. A Comparison of Oxide Thickness Data Obtained by Transmission Electron Microscopy and Multiple Beam Interferometry . . . . .	39
IV. CONCLUSIONS . . . . .	44

# LIST OF TABLES

Table		Page
I.	POLYPHENYLQUINOXALINE STRUCTURE AND PROPERTY INFORMATION . . . . .	4
II.	Ti-6Al-4V PREANODIZATION PROCEDURE . . . . .	6
III.	Ti-6Al-4V ANODIZATION METHODS FOR PPQ - Ti-6Al-4V BONDS . . . . .	9
IV.	POST-ANODIZATION Ti-6Al-4V CLEANING METHOD . . . . .	10
V.	TITANATE LIQUID PRIMER APPLIED TO THE CHROMIC ACID ANODIZED Ti-6Al-4V SURFACE . . . . .	11
VI.	PPQ STAGE DRY METHODS TO REMOVE SOLVENT AFTER PPQ APPLICATION TO CAA Ti-6Al-4V . . . . .	13
VII.	PPQ - CAA Ti-6Al-4V BONDING METHODS . . . . .	14
VIII.	Ti-6Al-4V CHROMIC ACID ANODIZATION METHODS AND OXIDE THICKNESS DATA USED FOR OXIDE ELECTRICAL PROPERTY ANALYSES . . . . .	19
IX.	POLYPHENYLQUINOXALINE/ANODIZED Ti-6Al-4V SINGLE LAP BOND STRENGTHS . . . . .	25
X.	Ti-6Al-4V ANODIZATION METHODS FOR PPQ - Ti-6Al-4V BONDS, AND OXIDE THICKNESS DATA . . . . .	26
XI.	THE INFLUENCE OF BONDING PROCEDURE ON POLYPHENYLQUINOXALINE/Ti-6Al-4V SINGLE LAP BOND STRENGTH . . . . .	27
XII.	TEST APPARATUS MEASUREMENTS AND THE MEASUREMENTS FOR TWO PARALLEL PLATE CAPACITORS IN SERIES WITH THE CAA OXIDE AS A DIELECTRIC . . . . .	30
XIII.	EQUATIONS TO DETERMINE PARALLEL PLATE CAPACITANCE . . . . .	31
XIV.	$C_x$ , PARALLEL PLATE CAPACITANCE WITH THE CAA OXIDE AS THE DIELECTRIC . . . . .	34
XV.	TEST APPARATUS MEASUREMENTS AND MEASUREMENTS FOR TWO PARALLEL PLATES IN SERIES WITH THE CAA/HF OXIDE BETWEEN THE PLATES. . . . .	36

## LIST OF FIGURES

Figure		Page
1.	SINGLE LAP BOND JOINT . . . . .	5
2.	SCHEMATIC OF ANODIZATION APPARATUS . . . . .	7
3(a).	TOP HALF OF BONDING JIG FOR SINGLE LAP BONDS . . . . .	15
3(b).	BOTTOM HALF OF BONDING JIG FOR SINGLE LAP BONDS . . . . .	16
4.	Ti-6Al-4V ANODIC OXIDE BULK RESISTIVITY DETERMINATION . . . . .	21
5.	SCHEMATIC OF CAPACITANCE MEASUREMENT TEST DESIGN FOR Ti-6Al-4V OXIDE . . . . .	22
6.	VOLTAGE VS. DISTANCE DATA USED IN BULK RESISTIVITY DETERMINATION FOR CAA/HF ANODIZATION PROCEDURE: 2.8 AMPERES/FT <sup>2</sup> INITIAL CURRENT DENSITY, 10V, 20 MINUTES, SOLUTION TEMPERATURE 25°C ± 2°C . . . . .	38
7.	TEM PHOTOGRAPH OF CAA/HF OXIDE ON Ti-6Al-4V SUBSTRATE IN CROSS SECTION (30,000X) CAA/HF ANODIZATION PROCEDURE: 2.0 AMPERES/FT <sup>2</sup> INITIAL CURRENT DENSITY, 10V, 20 MINUTES, SOLUTION TEMPERATURE 10°C ± 2°C . . . . .	40
8.	TEM PHOTOGRAPH OF CAA/HF OXIDE ON Ti-6Al-4V SUBSTRATE IN CROSS SECTION (200,000X) CAA/HF ANODIZATION PROCEDURE: 2.0 AMPERES/FT <sup>2</sup> INITIAL CURRENT DENSITY, 10V, 20 MINUTES, SOLUTION TEMPERATURE 10°C ± 2°C . . . . .	41
9.	TEM PHOTOGRAPH OF CAA/HF OXIDE ON Ti-6Al-4V SUBSTRATE IN PARALLEL SECTION (200,000X) CAA/HF ANODIZATION PROCEDURE: 2.0 AMPERES/FT <sup>2</sup> INITIAL CURRENT DENSITY, 10V, 20 MINUTES, SOLUTION TEMPERATURE 10°C ± 2°C . . . . .	42

## I. INTRODUCTION

The overall objectives of this research are as follows:

1. characterize the anodic oxide produced by chromic acid anodization of Ti-6Al-4V in terms of its anodic oxide thickness, surface ( $\leq 100 \text{ \AA}$ ) composition, morphology, structure and electrical properties,
2. characterize the unaged single lap bond strength of chromic acid anodized Ti-6Al-4V to the following heat resistant adhesives: a) unfilled polysulfone, b) unfilled polyphenylquinoxaline, c) filled polyimide, d) unfilled and filled polyetherimide, and e) unfilled polyethersulfone,
3. characterize the bond strengths after unstressed thermal aging for each adhesive cited above,
4. characterize the bond strengths after unstressed thermal aging for titanate primed chromic acid anodized Ti-6Al-4V which have been bonded bonded to selected adhesives cited above, and
5. vary the chromic acid anodization procedure and determine its influence upon the anodic oxide thickness, oxide electrical properties, and single lap bond strengths.

A status report<sup>(1)</sup> issued in December, 1984 and entitled "Characterization of Chromic Acid Anodized Ti-6Al-4V and Anodized Ti-6Al-4V Single Lap Bonds to Polysulfone" described the 1) anodic oxide thickness results obtained by multiple beam interferometry for selected chromic acid anodization procedures, 2) Electron

Spectroscopy for Chemical Analysis (ESCA) of the anodized Ti-6Al-4V surface, and 3) the unaged single lap bond strength, and bond strengths after unstressed thermal aging, for unfilled polysulfone bonds.

→ The purpose of this 1985 status report is to describe the:

1. morphology, thickness and structure characterization of chromic acid anodized Ti-6Al-4V determined by Transmission Electron Microscopy (TEM) and Selected Area Electron Diffraction (SAED);
2. unfilled polyphenylquinoxaline (PPQ) - chromic acid anodized (CAA) Ti-6Al-4V unaged single lap bond strength data;
3. unstressed thermal aging tests in progress for PPQ - CAA Ti-6Al-4V single lap bonds, and
4. tests in progress to determine the electrical properties of CAA Ti-6Al-4V; these tests will determine the anodic oxide capacitance, dielectric constant and bulk resistivity.

## II. EXPERIMENTAL

### A. Polyphenylquinoxaline - Chromic Acid Anodized Single Lap Bonds

#### i. Materials

The unfilled thermoplastic used in the single lap bonds was polyphenylquinoxaline (PPQ) dissolved in a 1:1 xylene:cresol diluent. The PPQ was supplied by Paul Hergenrother of NASA Langley. PPQ structure and property information is described in Table I. The PPQ was stored 9 months at 5°C prior to its use.

The metal used in the single lap bonds was Ti-6Al-4V. The dimensions of the Ti-6Al-4V coupons are described in Figure 1.

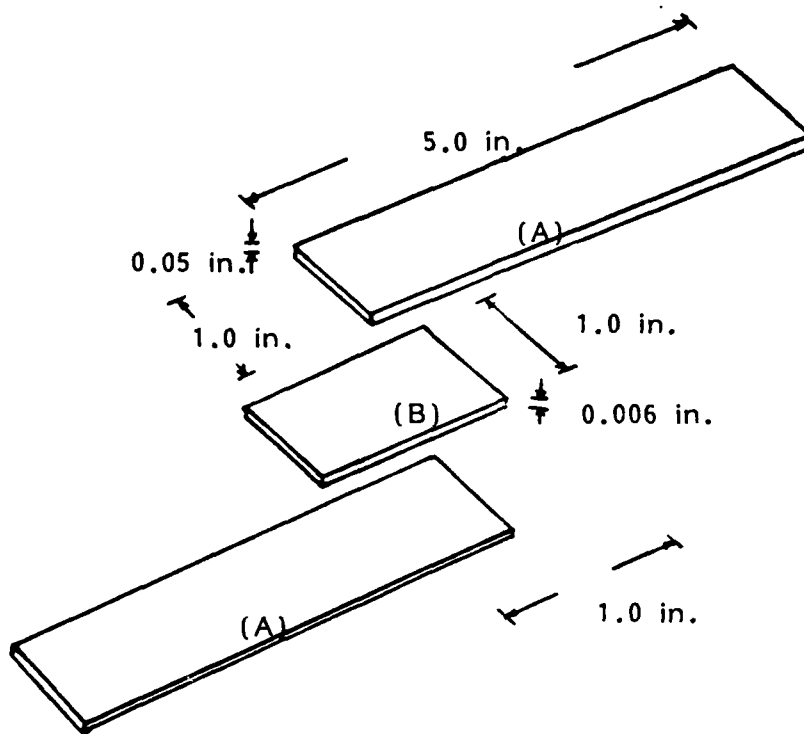
#### ii. Anodization Method

The Ti-6Al-4V coupons were 1,1,1 trichloroethane vapor degreased in a standard degreaser set-up. The vapor degreaser cleaning schedule used was: 15 minutes in the vapor of a 52°C solvent sump, 5 minutes immersed in 25°C solvent, followed by another 5 minutes in the solvent vapors. The 1,1,1 trichloroethane cleaning procedure removes the organic contamination. This cleaning procedure is a standard industrial method used for cleaning metals and is comparable to the trichlorethylene method described in the 1984 report.<sup>(1)</sup>

After vapor degreasing, the Ti-6Al-4V coupons were pickled to remove the natural oxide. The procedure is described in Table II. The coupons were then anodized; the anodization apparatus is illustrated in Figure 2. A 750 cc, 5% solution of  $\text{CrO}_3$  was used to anodize 6 coupons connected in a parallel circuit. A 50% hydrofluoric acid was added to the anodization solution in a 0.3% V/V to obtain the



Figure 1. Single Lap Bond Joint



(A) ANODIZED Ti-6Al-4V COUPON

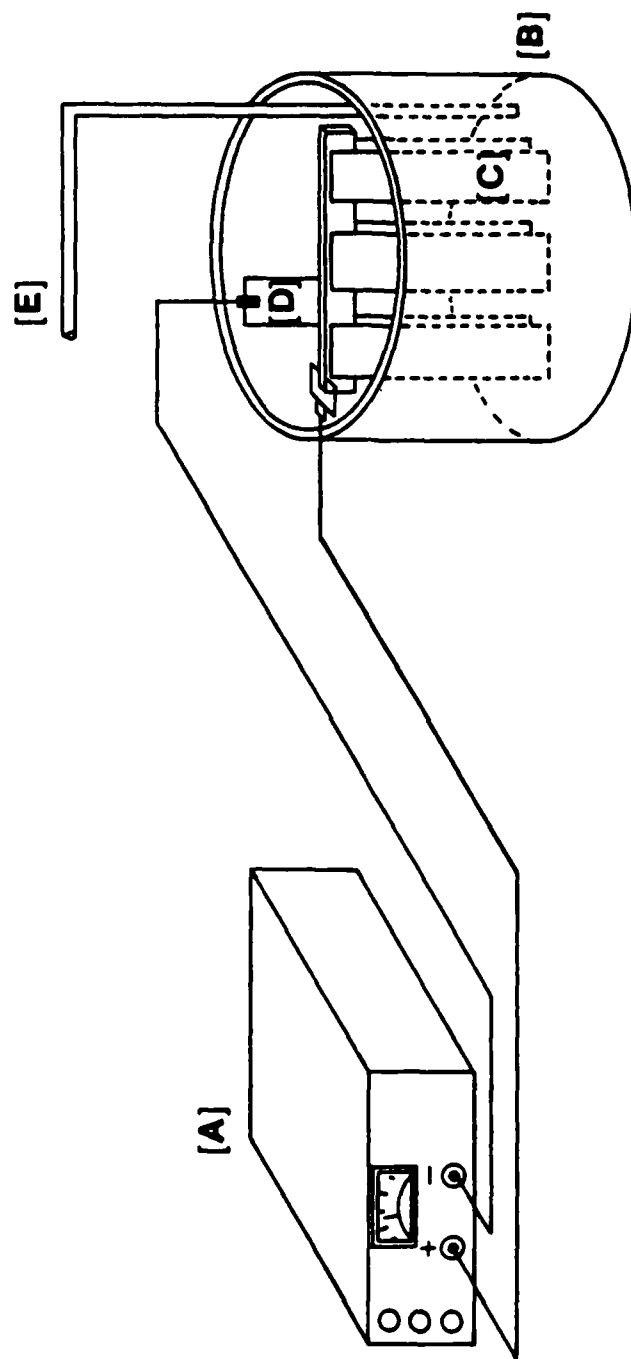
(B) POLYPHENYLQUINOXALINE THERMOPLASTIC

TABLE II

## Ti-6Al-4V PREANODIZATION PROCEDURE

1. Vapor degrease in 1,1,1 Trichloroethane.
2. Pickle 30 seconds in a deionized, distilled water solution of 15% volume of 70%  $\text{HNO}_3$  and 3% volume of 49% HF.
3. Immerse coupons 5 minutes in 500 ml distilled, deionized water.
4. Repeat Step #3.
5. Nitrogen dry.

Figure 2. SCHEMATIC OF ANODIZATION APPARATUS



- [A] CONSTANT VOLTAGE POWER SUPPLY
- [B] TEFLON ANODIZATION TANK
- [C] ANODES CONNECTED IN PARALLEL
- [D] CATHODE
- [E] TEFLON TUBE [ FOR AIR AGITATION OF SOLUTION ]

desired initial current density at 10V. The anodization cathode was a Ti-6Al-4V coupon, also. Distilled, deionized water was used in all solutions.

Three anodization procedures were tested and are described in Table III. These procedures varied the anodization temperature and current density. Anodization was conducted at  $10^{\circ}\text{C} \pm 2^{\circ}\text{C}$  at either 2.0 Amperes/ft<sup>2</sup> or 2.8 Amperes/ft<sup>2</sup> initial current density. Also, anodization was conducted at an initial current density of 2.8 Amperes/ft<sup>2</sup> and  $25^{\circ}\text{C} \pm 2^{\circ}\text{C}$ . After anodization, the coupons were soaked in distilled, deionized water and nitrogen dried as described in Table IV.

iii. Titanate Primer Application Method for CAA/HF Ti-6Al-4V

Some of the CAA Ti-6Al-4V coupons were primed with Lica 44, a neoalkoxy primer, prior to application of the PPQ. The Lica 44 was supplied by Kenrich Petrochemicals, Inc. and the structure is illustrated in Table V. Lica 44 is a neoalkoxy, tri (N ethylamino-ethylamino) titanate.

This titanate, in a monolayer coverage, is considered beneficial for adhesion of the metal oxide to the thermoplastic. The RO moiety of the Lica 44 structure bonds with the inorganic metal oxide while the amine terminated end of the titanate provides van der Waals' entanglement with the PPQ thermoplastic.

A 0.2% V/V Lica 44 in reagent grade isopropanol was applied to the anodized Ti-6Al-4V substrate with a sponge brush. The primed Ti-6Al-4V was then stage dried at  $65^{\circ}\text{C}$  for 0.5 hr.

TABLE III  
Ti-6Al-4V ANODIZATION METHODS FOR PPQ - Ti-6Al-4V BONDS

<u>METHOD</u>	<u>CAA TIME (MINUTES)</u>	<u>WITH OR WITHOUT HF</u>	<u>TEMPERATURE (°C)</u>	<u>CURRENT (AMPERES/FT<sup>2</sup>)</u>	<u>VOLTAGE</u>
#1	20	WITH	10	2.0	10
#2	20	WITH	25	2.8	10
#3	20	WITH	10	2.8	10

TABLE IV

## POST-ANODIZATION Ti-6Al-4V CLEANING METHOD

1. Soak in a 500 ml volume distilled, deionized water 2 minutes.
2. Soak in a clean 500 ml volume distilled, deionized water 2 minutes.
3. Soak in a clean 500 ml volume of distilled, deionized water 15 minutes.
4. Repeat Steps #1 and #2.
5. Nitrogen dry.

NOTE: This procedure is used for cleaning six coupons simultaneously. The coupons were immersed so as to clean the 1 square inch of anodized surface area.

TABLE V

TITANATE LIQUID PRIMER APPLIED TO THE  
CHROMIC ACID ANODIZED Ti-6Al-4V SURFACE

VENDOR NAME: LICA 44

CHEMICAL NAME: neoalkoxy, tri(N ethylaminoethylamino) titanate

CHEMICAL  
STRUCTURE:  $\text{RO-Ti}(\text{O-C}_2\text{H}_4\text{-NH-C}_2\text{H}_4\text{-NH}_2)_3$

DILUTION USED: 0.2%, BY VOLUME, LICA 44 IN REAGENT  
GRADE ISOPROPYL ALCOHOL

#### iv. Single Lap Bond Assembly Technique

The PPQ adhesive was applied to the CAA Ti-6Al-4V within one hour after anodization. The PPQ temperature was allowed to equilibrate at  $25^{\circ}\text{C} \pm 2^{\circ}\text{C}$  before opening the container so as to prevent moisture condensation.

The PPQ was applied with a micrometer-adjusted blade to allow uniform adhesive thickness. The PPQ was applied in a 4 mil thick layer and stage dried in clean ovens as described in Table VI. The stage drying reduced the 4 mil PPQ thickness by approximately 50% as measured with micrometers. The coupons were then cooled to  $25^{\circ}\text{C} \pm 2^{\circ}\text{C}$  and another 4 mil thick PPQ layer was applied and stage dried. The final PPQ thickness on each coupon was  $6 \text{ mil} \pm 1 \text{ mil}$ .

The PPQ - Ti-6Al-4V coupons were bonded in single lap bonds within six hours of PPQ application. The bonds were formed by either an isothermal or isochronal bonding process as described in Table VII.

The isothermal process was per communication with Paul Hergenrother. The isochronal process was based upon a reported method,<sup>(2)</sup> with two exceptions. A 6000 psi bonding pressure was used rather than the reported literature value of 200 psi. A  $399^{\circ}\text{C}$  bonding temperature was used rather than the  $316^{\circ}\text{C}$  reported literature value. Reasons for these differences will be discussed in the Results and Discussion section.

The bond configuration and adhesive thickness were controlled during bonding by positioning the PPQ - Ti-6Al-4V coupons in an aluminum alloy jig. A schematic of the jig is illustrated in Figure 3a

TABLE VI

PPQ STAGE DRY METHODS TO REMOVE SOLVENT AFTER PPQ APPLICATION  
TO CAA Ti-6Al-4V

1. Dry coupons 30 minutes in a  $100^{\circ}\text{C} \pm 5^{\circ}\text{C}$  clean oven.
2. Dry coupons 30 minutes in a  $160^{\circ}\text{C} \pm 10^{\circ}\text{C}$  clean oven.
3. Dry coupons 30 minutes in a  $200^{\circ}\text{C} \pm 10^{\circ}\text{C}$  clean oven.

TABLE VII

## PPQ - CAA Ti-6Al-4V BONDING METHODS

ISOTHERMAL BONDING PROCESS

1. Place coupons in bonding jig and insert jig in platen press which has been preheated to 371°C. Heat jig for 3 minutes at 371°C.
2. Apply 200 psi at 371°C and hold pressure and temperature for 5 minutes.
3. Cool jig under pressure until platen press is less than 150°C.
4. Remove jig from platen press.

ISOCHRONAL BONDING PROCESS

1. Place stage dried PPQ - CAA Ti-6Al-4V coupons in vacuo at 180°C for 24 hours.
2. Place coupons in bonding jig and insert jig in platen press at room temperature.
3. Apply 200 psi and heat to 399°C over a 90 minute period.
4. Increase pressure to 6000 psi at 399°C and hold for 1 minute.
5. Reduce pressure to 200 psi at 399°C and hold for 30 minutes.
6. Cool jig under pressure until platen press is less than 150°C.
7. Remove jig from platen press.

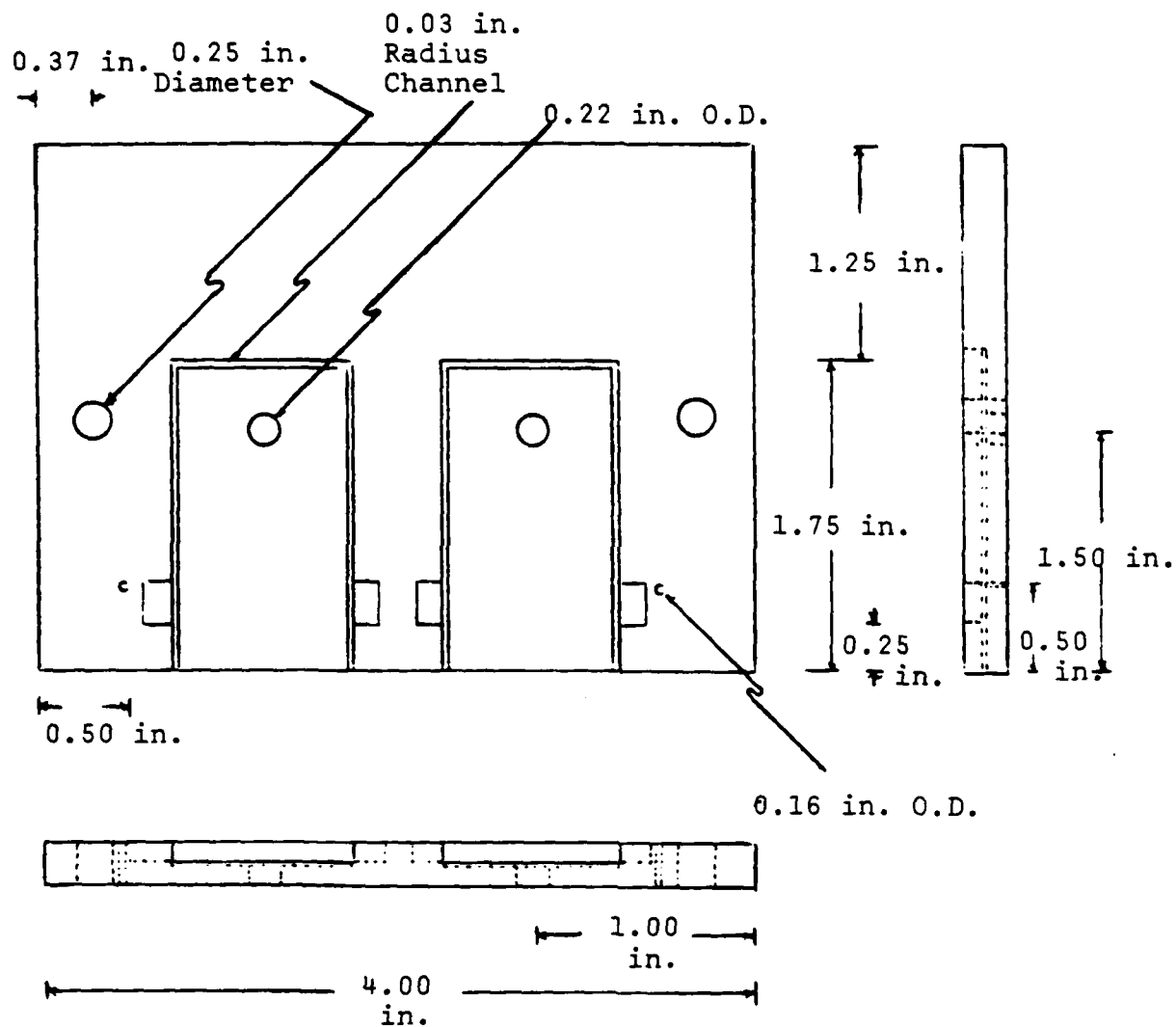


Figure 3a. TOP HALF OF BONDING JIG FOR SINGLE LAP BONDS

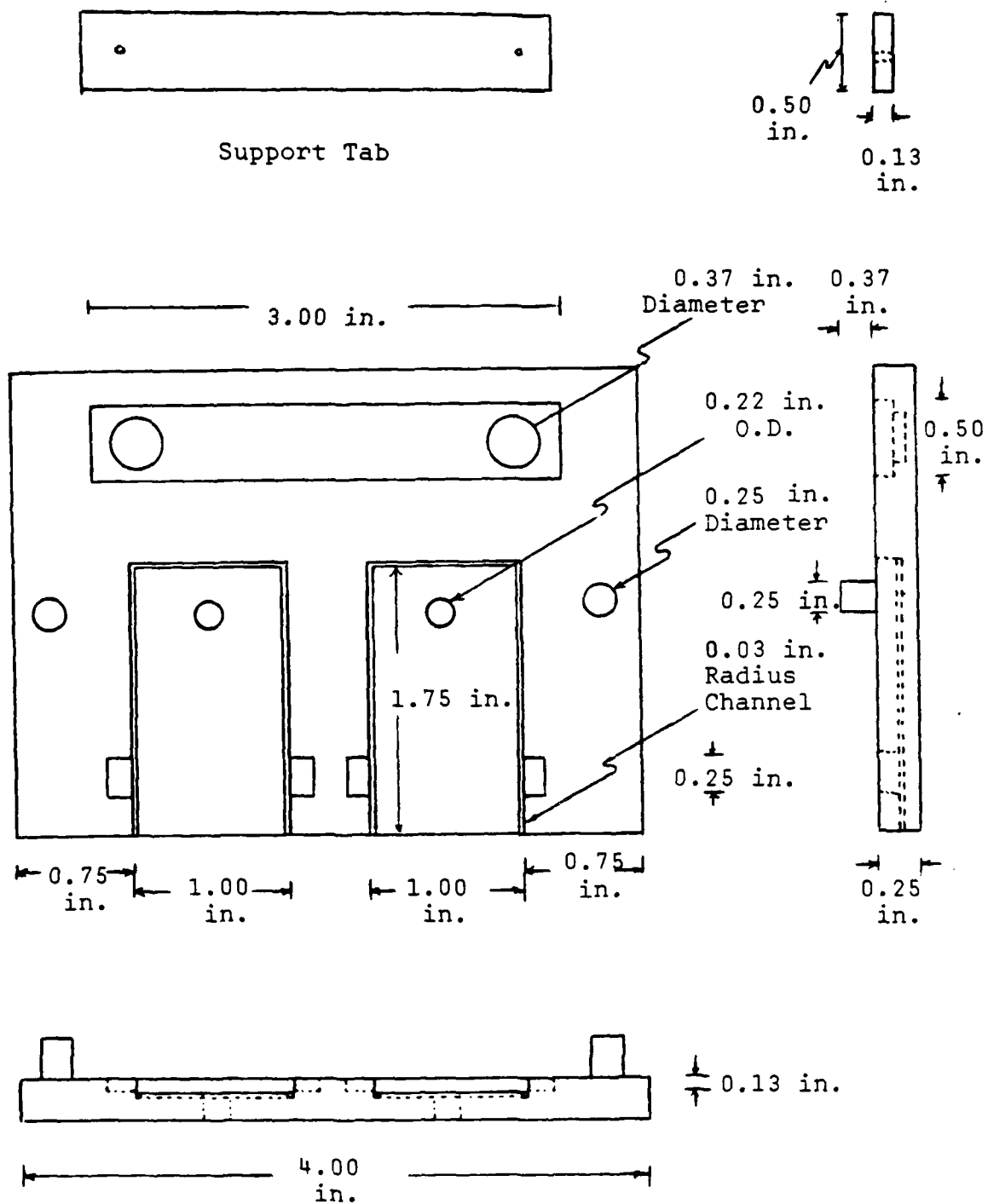


Figure 3b. BOTTOM HALF OF BONDING JIG FOR SINGLE LAP BONDS

and Figure 3b. The jig was lined with 0.9 mil thick aluminum foil for protection. Aluminum inserts, 19 mil thick, were placed in the jig channels to maintain the desired  $6 \pm 1$  mil bond line thickness.

The single lap bond configuration was per ASTM D1002 entitled "Strength Properties of Adhesives in Shear by Tension Loading (Metal-to-Metal)." The joint design is illustrated in Figure 1.

#### v. Bondline Thickness Measurements

A Unitron metallograph microscope with a camera attachment was used to photograph the PPQ bondline for adhesive thickness measurement. Three sections, each 7 mil long, were photographed along a bondline. Three single lap bond joints were measured per this method. The bondline thickness was  $6 \pm 1$  mil.

#### vi. Single Lap Bond Shear Strength Test Method

The single lap bond shear strength was tested by tension loading per ASTM D1002. Bonds were tested unaged, i.e. between two and seven days after bonding. Prior to shear testing, these bonds were stored in ambient conditions.

#### vii. Single Lap Bond Thermal Aging Tests

PPQ - CAA Ti-6Al-4V single lap bonds, which were anodized per the first method described in Table III and bonded per the isothermal process, were subjected to unstressed thermal aging. Six bonds were subjected to each of the following conditions:

- 1)  $25^{\circ}\text{C} \pm 5^{\circ}\text{C}$ , 45 to 60% relative humidity, for 9 months,
- 2)  $170^{\circ}\text{C} \pm 5^{\circ}\text{C}$  for 9 months, and
- 3)  $232^{\circ}\text{C} \pm 10^{\circ}\text{C}$  for 9 months.

These thermal aging tests are currently in progress.

In addition, LICA 44 primed Ti-6Al-4V - PPQ bonds are being

thermally aged at 170°C for 9 months prior to bond strength tests.

#### B. Transmission Electron Microscopy (TEM) and Selected Area Electron Diffraction (SAED) Analyses

A 1.5 mil thick Ti-6Al-4V foil was purchased from Arnold Subsidiary Magnetics and Electronics, Inc. The foil was vapor degreased and pickled as described earlier, and then anodized per the first method described in Table III. The TEM and SAED analyses of the foil were conducted at Structure Probe, Inc., of West Chester, Pennsylvania.

At Structure Probe, Inc. the foil was embedded in an epoxy and microtomed to produce ultrathin cross sections and parallel sections of the film. The foil to be cross sectioned was gold sputtered prior to epoxy embedding. TEM analyses of the oxide cross section were conducted to elucidate the oxide roughness, morphology and thickness. TEM analyses of the oxide in parallel section were conducted to elucidate oxide morphology. The parallel sections were also analyzed by SAED to determine oxide structure.

#### C. CAA Ti-6Al-4V Oxide Electrical Properties

##### i. Methods and Materials

The dielectric constant, capacitance and bulk resistivity determination for the CAA Ti-6Al-4V oxide are currently in progress. These oxide electrical properties are being determined as a function of the CAA procedures described in Table VIII.

The oxide thickness data, necessary for the determination of oxide electrical properties, are also reported in Table VIII. The oxide thickness data were determined by multiple beam interferometry as described in the 1984 report.<sup>(1)</sup>

TABLE VIII

Ti-6Al-4V CHROMIC ACID ANODIZATION METHODS AND OXIDE THICKNESS DATA  
USED FOR OXIDE ELECTRICAL PROPERTY ANALYSES

METHOD	BATH COMPOSITION	BATH TEMPERATURE (°C)	ANODIZATION INITIAL		ANODIZATION VOLTAGE (VOLTS)	ANODIZATION TIME (MINUTES)	OXIDE THICKNESS (nm/ μin)
			CURRENT DENSITY (AMPERES/FT <sup>2</sup> / mAMPERES/CM <sup>2</sup> )				
1	5% Chromic Acid Solution w/ HF	25	2.8/3.0		10	20	140/5.5 <sup>(1)</sup>
2	Same as above	25	2.8/3.0		10	60	290/11.3 <sup>(1)</sup>
3	5% Chromic Acid Solution w/o HF	25	2.8/3.0		39	20	20/0.8 <sup>(1)</sup>
4	5% Chromic Acid Solution w/ HF	10	2.8/3.0		10	20	410/16.0 <sup>(1)</sup>
5	5% Chromic Acid Solution w/ HF	10	2.0/2.1		10	20	160/6.3 <sup>(1)</sup> 95-150/3.7-5.8 <sup>(2)</sup>

NOTES: (1) Measured by interferometry. Accuracy is  $\pm 10$  nm (0.4 μin.).  
(2) Measured by TEM analysis.

The electrical property measurements were conducted at  $25^{\circ}\text{C} \pm 2^{\circ}\text{C}$  in a nitrogen environment. Contact probes for these measurements were designed to apply 3 ounces of force to the oxide surface.

## ii. Bulk Resistivity Determination

In order to determine oxide bulk resistivity, approximately 70 nm of pure silver was evaporated onto the anodized Ti-6Al-4V surface as equidistantly spaced rectangles by means of a template as shown in Figure 4.

The oxide bulk resistivity determination is also described in Figure 4. A known current and voltage was applied to the silver rectangles at each end of the sample. The potential was measured as a function of distance, relative to the end rectangle. The rectangular geometry insured equal potential between the silver deposits.

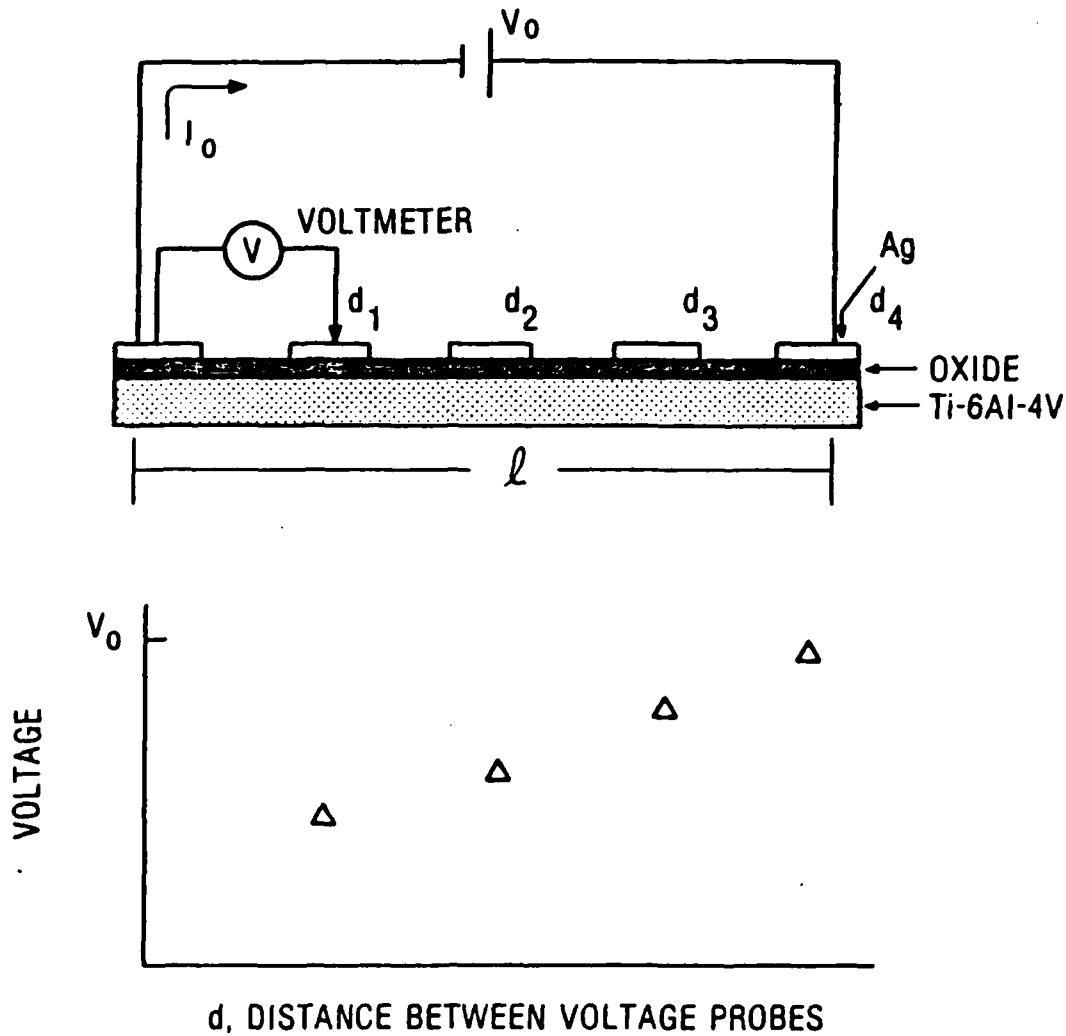
Based upon the applied current, the slope of the potential distance data, and the distance between the end rectangles,  $l$ , the bulk resistance,  $R$ , was calculated. The oxide cross-sectional area was then calculated based upon a single rectangle length and the oxide thickness data. The oxide bulk resistivity,  $P$ , was then calculated by:

$$P = \frac{R A}{l} \quad [1]$$

## iii. Capacitance Measurements

Capacitance measurements, with the oxide as the dielectric, were determined as described in Figure 5. Silver disks approximately 70 nm thick were evaporated onto the anodized Ti-6Al-4V surface by means of a template. The geometry of the silver disks was chosen so as to minimize electrical field edge effects in the capacitance measurements.

Figure 4. Ti-6Al-4V ANODIC OXIDE BULK RESISTIVITY DETERMINATION

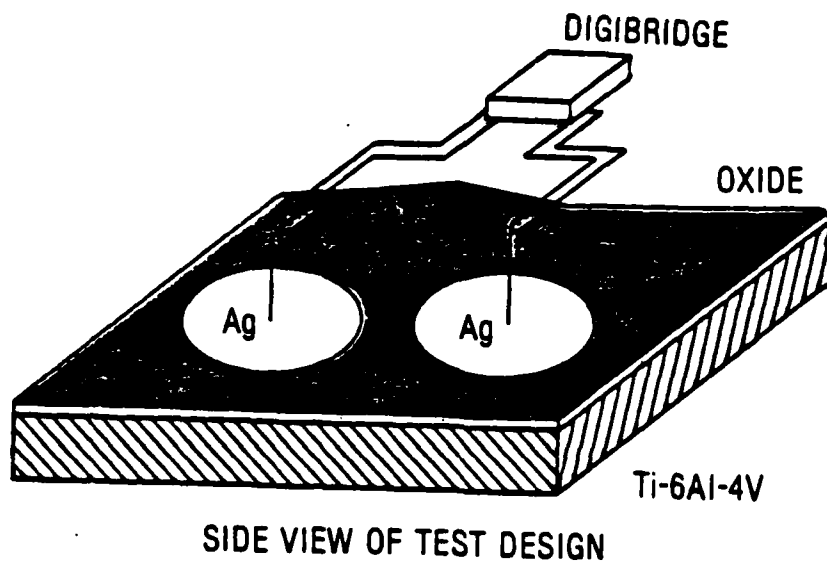


$R$ , oxide bulk resistance, is calculated based upon: the known applied current,  $I_0$ , the slope of the voltage vs. distance graph, and the distance between end voltage probes,  $\ell$ . The oxide bulk resistivity,  $\rho$ , is calculated by:

$$\rho = \frac{RA}{\ell}$$

where  $A$  is the cross-sectional area of the oxide.

Figure 5. SCHEMATIC OF CAPACITANCE MEASUREMENT TEST DESIGN FOR Ti-6Al-4V OXIDE.



An evaporated disk, oxide and metal substrate form a parallel plate capacitor. Capacitance for two parallel plate capacitors in series was measured at 1 MHz, 1 KHz and 120 Hz. A GR 1687-B LC Digibridge<sup>®</sup> impedance meter from GenRad, Inc. was used for capacitance measurements at 1 MHz. A GR 1657 RLC Digibridge<sup>®</sup> from GenRad, Inc. was used for capacitance measurements at 1 KHz and 120 Hz.

Capacitance measurements were made for at least four different adjacent silver disks for each type of anodic oxide. Stray capacitance or inductance from the probe apparatus was subtracted from the capacitance measurements to determine the actual parallel plate capacitance with the oxide as the dielectric. Stray capacitance or inductance from the probe apparatus was measured by placing the measurement probe apparatus on a brass coupon which had been scrubbed immediately prior to measurements so as to remove any oxide.

#### iv. Oxide Dielectric Constant Determination

The oxide dielectric constants at 1 MHz, 1 KHz and 120 Hz were calculated based upon the capacitance measurements at each respective frequency. The oxide dielectric constant can be determined for a parallel plate capacitor by using the following relationship:

$$C = \frac{E_0 K A}{d} \quad [2]$$

where  $E_0$  is the permittivity of free space,  $3.48 \times 10^{-14}$  Farads per inch ( $8.85 \times 10^{-12}$  Farads per meter),  $K$  is the dielectric constant,  $C$  is the measured capacitance,  $A$  is the measured area of one silver disk and  $d$  is the oxide thickness.

### III. RESULTS AND DISCUSSION

#### A. PPQ - CAA Ti-6Al-4V Unaged Single Lap Bond Strength

The average PPQ single lap bond strengths as a function of the Ti-6Al-4V CAA procedure are described in Table IX. Each average represents six bonds. These data are for bonds produced per the isothermal process.

The average bond strength data ranges from  $4480 \pm 520$  psi to  $5500 \pm 770$  psi. These strength data are comparable to other reported values for PPQ bonds.<sup>(2), (3)</sup>

No significant differences in single lap bond strengths were observed as a function of the anodization solution temperature and the initial current densities investigated. It should be noted that the oxide thickness varied from 95 to 410 nm ( $3.71 \times 10^{-6}$  in. to  $1.6 \times 10^{-5}$  in.), as a function of the CAA procedure, as shown in Table X.

Table XI compares the average PPQ single lap bond strength of isothermal and isochronal processed bonds. The Ti-6Al-4V CAA procedure was held constant and is described in Method 1 shown in Table III. There are two obvious differences between the isothermal and isochronal processed bond strength data. First, the average isothermal processed bond strength was approximately 81% higher than the average isochronal processed bond strength. Secondly, the isothermal processed bond failure mode was predominantly in the PPQ adhesive, based on visual analysis. In contrast, for the isochronal processed bonds, the anodic blue oxide separated from the Ti-6Al-4V surface. This apparent oxide-metal failure was only observed for isochronal processed bonds.

TABLE IX

## POLYPHENYLQUINOXALINE/ANODIZED Ti-6Al-4V SINGLE LAP BOND STRENGTHS

## METAL PREANODIZATION AND ANODIZATION TREATMENT

CAA TIME (MINUTES)	WITH OR WITHOUT HF	TEMP. (°C)	CURRENT (AMPERES/ SQ. FT.)	AVERAGE BOND		STANDARD DEVIATION
				VOLTAGE (VOLTS)	STRENGTH (PSI)	
20	WITH	10	2.0	10	4750	280
20	WITH	25	2.8	10	5500	770
20	WITH	10	2.8	10	4480	520

BONDING PROCESS WAS: THREE MINUTE PREHEAT AT 371°C,  
FOLLOWED BY FIVE MINUTES AT 371°C UNDER  
A PRESSURE OF 200 PSI. COOLED UNDER PRESSURE  
TO 150°C BEFORE RELEASING PRESSURE.

AVERAGE ADHESIVE THICKNESS MEASURED FOR SINGLE LAP BOND  
WAS  $0.006 \pm 0.001$  INCH.

TABLE X  
Ti-6Al-4V ANODIZATION METHODS FOR PPQ - Ti-6Al-4V BONDS, AND OXIDE THICKNESS DATA

METHOD	CAA TIME (MINUTES)	WITH OR WITHOUT HF	TEMPERATURE (°C)	CURRENT		VOLTAGE (VOLTS)	OXIDE THICKNESS (nm/ $\mu$ in)
				(AMPERES/FT <sup>2</sup> / AMPERES/CM <sup>2</sup> )			
#1	20	WITH	10	2.0/2.1		10	95-150/3.7-5.8 <sup>(2)</sup> 161/6.3 <sup>(1)</sup>
#2	20	WITH	25	2.8/3.0		10	140/5.5 <sup>(1)</sup>
#3	20	WITH	10	2.8/3.0		10	410/16.0 <sup>(1)</sup>

NOTES: (1) Measured by Interferometry. Accuracy is  $\pm 10$  nm (0.4  $\mu$ in.).  
(2) Measured by TBM analysis.

TABLE XI

## THE INFLUENCE OF BONDING PROCEDURE ON

## POLYPHENYLQUINOXALINE/Ti-6Al-4V SINGLE LAP BOND STRENGTH

<u>BONDING PROCESS</u>	<u>AVERAGE BOND STRENGTH STANDARD (PSI)</u>	<u>DEVIATION</u>	<u>VISUAL FAILURE ANALYSIS</u>
ISOTHERMAL PROCESS:			
3 MINUTE PREHEAT AT 371°C, FOLLOWED BY 5 MINUTES AT 371°C, 200 PSI.	4750	280	THERMOPLASTIC CO-HESIVE FAILURE
ISOCHRONAL PROCESS:			
VACUUM BAKE COUPONS 24 HRS. AT 180°C. BOND AT 200 PSI, 25°C TO 399°C IN 90 MINUTES. AT 399°C, INCREASED PRESSURE TO 6000 PSI AND HOLD FOR 1 MINUTE. REDUCED PRESSURE TO 200 PSI; HOLD FOR 30 MIN.	2630	200	ADHESIVE FAILURE OF ANODIC FILM TO THE BARE METAL

- NOTES: (1) Ti-6Al-4V ANODIZATION PROCEDURE USED FOR BOTH BONDING PROCEDURES WAS: 2.0 AMPERES/FT<sup>2</sup>, 10°C, 20 MINUTES, CAA WITH HF SOLUTION.
- (2) SAMPLE SIZE FOR ISOCHRONAL PROCESS WAS 4 BOND PAIRS. ISOTHERMAL SAMPLE SIZE WAS 6 BOND PAIRS.

The relatively low bond strength and apparent oxide-metal failure mode for the isochronal bonding process are attributed to both the high bonding pressure, 6000 psi, and prolonged high temperature exposure, 399°C, for thirty minutes. The isochronal bonding pressure was thirty times higher and the bonding temperature was 83°C higher than is typical for isochronal bonding.<sup>(2)</sup>

The higher pressure and temperatures were necessary to mate the two halves of the bonding jig. This was because the isochronal vacuum stage drying caused hard, elevated areas in the PPQ, apparently the result of solvent evacuation during drying in vacuo.

The high temperature and pressure used in the isochronal bonding process could have caused the residual cresol and xylene PPQ diluents to more effectively penetrate and separate the oxide from the metal. This would explain the observed metal-oxide bond failure at low stress.

The diluent penetration effect has been proposed by Carl Hendricks, et al<sup>(3)</sup> to explain the oxide separation and relatively low PPQ bond strength, 2900 psi, which he observed for CAA Ti-6Al-4V bonds. In this study, the bonds were processed isothermally at 375°C for 60 minutes. It was recommended that PPQ bond processing should not exceed 15 minutes at 375°C in order to prevent the metal-oxide failure and low bond strengths.

#### B. PPQ - CAA Ti-6Al-4V Single Lap Bond Strength After Unstressed Thermal Aging

The unstressed thermal aging tests for PPO - CAA Ti-6Al-4V, which are described in the Experimental section, are currently in progress. These data will be included in a later report.

The CAA anodization procedure used is described as Method 1 in Table III. The 10°C solution temperature, rather than the 25°C temperature, was chosen to minimize Joule heating of the oxide microstructure and oxide flaws during anodization.

### C. Electrical Properties of Anodic Oxide Produced by CAA Without HF

The oxide under study was produced by anodization without hydrofluoric acid (HF) and is described as method #3 in Table VIII.

#### i. Capacitance of Oxide Produced by CAA Without HF

Table XII contains the measured inductance for the test apparatus,  $L_{ts}$ . Test apparatus measurements were made before and after each oxide measurement; these values remained constant. Table XII also contains the measurements for the two parallel discs tested in series with the anodic oxide as the dielectric. All measurements were conducted in dry nitrogen at  $25^{\circ}\text{C} \pm 2^{\circ}\text{C}$ .

It can be seen in Table XII that the test apparatus and the sample were capacitive. By knowing the inductance of the test apparatus,  $L_{ts}$ , the capacitance of the sample plus test apparatus,  $C_t$ , and the frequency,  $w$ , then the parallel plate capacitance with the CAA oxide as a dielectric,  $C_x$ , can be calculated. This calculation is described in Table XIII.

In the oxide capacitance calculations described in Table XIII, it is assumed that the stray capacitance between any pair of silver disks in the measurement circuit is low, and the stray capacitance does not contribute significantly to the oxide capacitance. This assumption is based upon the small distance, i.e. less than 16  $\mu\text{in}$ . (410 nm), from one silver disk to the metal substrate, compared to the relatively

TABLE XII

TEST APPARATUS MEASUREMENTS AND THE MEASUREMENTS FOR TWO  
PARALLEL PLATE CAPACITORS IN SERIES WITH THE CAA OXIDE  
AS A DIELECTRIC

<u>Frequency</u>	<u>Test Apparatus (Henries)</u>	<u>Test Apparatus and Sample (Farads)</u>
120 Hz	0	$159.71 \times 10^{-6}$
	0	$149.49 \times 10^{-6}$
	0	$128.11 \times 10^{-6}$
	0	$169.14 \times 10^{-6}$
1 KHz	$300.00 \times 10^{-9}$	$152.07 \times 10^{-6}$
	$300.00 \times 10^{-9}$	$180.00 \times 10^{-6}$
	$300.00 \times 10^{-9}$	$34.40 \times 10^{-6}$
	$300.00 \times 10^{-9}$	$13.85 \times 10^{-6}$
1 MHz	$254.00 \times 10^{-9}$	$190.72 \times 10^{-11}$
	$208.00 \times 10^{-9}$	$730.80 \times 10^{-12}$
	$190.00 \times 10^{-9}$	$390.30 \times 10^{-12}$
	$190.00 \times 10^{-9}$	$655.84 \times 10^{-12}$

NOTES: (1) Oxide was electrodeposited onto Ti-6Al-4V by CAA method #3 described in Table VIII.

(2) Each test apparatus measurement was for a specific pair of probes. Each test apparatus datum in Column 2 corresponds specifically to the adjacent datum in Column 3.

TABLE XIII

## EQUATIONS TO DETERMINE PARALLEL PLATE CAPACITANCE

Test Conditions: Test apparatus is inductive. Test apparatus plus two parallel plate capacitors test in series are capacitive.

Definitions:  $Z$  = impedance

$R_t$  = test apparatus resistance

$X_t$  = complex reactance of test apparatus plus two parallel plate capacitors in series

$X_{ts}$  = complex reactance of test apparatus

$X = X_t - X_{ts}$

$w = 2\pi f$

$f$  = frequency, in Hz

$C_t$  = capacitance of test apparatus plus two parallel plate capacitors in series

$C_{ts}$  = capacitance of the test apparatus

$C_s$  = capacitance of two parallel plate capacitors in series

$C_x = 2C_s$  = Capacitance of one parallel plate capacitor

$L_t$  = inductance of test apparatus plus two parallel plate capacitors in series

$L_{ts}$  = inductance of the test apparatus

$j = -1 = 1/j$

Equations:

$$[1] \quad Z = R_t - R_{ts} + X_t - X_{ts}$$

$$[2] \quad X_t = -j/wC_t \text{ or } X_t = jwL_t$$

$$X_{ts} = -j/wC_{ts} \text{ or } X_{ts} = jwL_{ts}$$

$$[3] \quad X = X_t - X_{ts}$$

TABLE XIII (Continued)

$$[4] \quad X = -j(1/wC_t + wL_{ts})$$

$$[5] \quad X = 1/jwC_s$$

$$[6] \quad 1/jwC_s = -j(1/wC_t + wL_{ts})$$

[7] Once the vector direction has been determined by the sign on  $j$ , then only the vector magnitude need be considered in the capacitance calculation.

$$1/wC_s = 1/wC_t + wL_{ts}$$

$$[8] \quad 1/C_s = 1/C_t + w^2L_{ts}$$

$$[9] \quad C_s = 1/(1/C_t + w^2L_{ts})$$

$$[10] \quad C_s = C_t/(1 + w^2L_{ts}C_t)$$

$$[11] \quad C_x = 2C_s$$

large 0.148 in. center to center distance between adjacent disks.

Parallel plate capacitance with the CAA oxide as the dielectric is shown in Table XIV for 120 Hz, 1 KHz, and 1 MHz. The trend indicated by this data appears to show that as frequency is increased, parallel plate capacitance decreased. Apparently, as frequency is increased, the alignment of the polarizable oxide between the oppositely charged metal substrates is disrupted, thereby reducing oxide capacitance.

Variations in the parallel plate capacitance at any one frequency may be attributed in part to variations in the oxide thickness. These variations in oxide thickness will be discussed later, in section F, of this report.

#### ii. Dielectric Constant of Oxide Produced by CAA Without HF

The CAA oxide dielectric constant was calculated based upon the capacitance data as previously described in Table XII, and the 0.8  $\mu$ in. (20 nm) oxide thickness determined by interferometry.

The average dielectric constant at 1 MHz was 0.88. This calculation was based upon four capacitance measurements at 1 MHz. The average dielectric constant ranged from 1.5 to 0.2 based upon one standard deviation of the four capacitance measurements.

#### iii. Bulk Resistivity of Oxide Produced by CAA Without HF

The CAA oxide bulk resistivity determination is currently in progress and will be reported in a later report.

### D. Electrical Properties of Anodic Oxide Produced by CAA With HF

The oxide under study was produced by anodization with hydrofluoric acid (HF) and is described as method #1 in Table VIII.

TABLE XIV

$C_x$ , PARALLEL PLATE CAPACITANCE WITH THE CAA OXIDE  
AS THE DIELECTRIC

Frequency	$C_x$ (Farads)
120 Hz	$3.20 \times 10^{-4}$
	$3.00 \times 10^{-4}$
	$2.60 \times 10^{-4}$
	$3.40 \times 10^{-4}$
1 KHz	$3.04 \times 10^{-4}$
	$3.59 \times 10^{-4}$
	$6.88 \times 10^{-5}$
	$2.77 \times 10^{-5}$
1 MHz	$3.74 \times 10^{-9}$
	$1.46 \times 10^{-9}$
	$0.78 \times 10^{-9}$
	$1.30 \times 10^{-9}$

NOTE:  $C_x$  calculations were based upon equations in Table XIII,  
and data measured at  $25^\circ\text{C} \pm 2^\circ\text{C}$  in a dry nitrogen  
environment as shown in Table XII.

i. Capacitance of Oxide Produced by CAA with HF

The test data for two parallel plates tested in series with the oxide as the dielectric are shown in Table XV. The data for the test apparatus are also included in Table XV.

It can be seen that the CAA/HF oxide is neither capacitive nor inductive at 1 MHz, 1 KHz, or 120 Hz. At 1 MHz, the test apparatus inductance,  $L_{ts}$ , was greater than the inductance of the test apparatus plus oxide,  $L_t$ . At 1 KHz and at 120 Hz, the test apparatus inductance,  $L_{ts}$ , was equal to the inductance of the test apparatus plus oxide sample,  $L_t$ .

The electrical properties of this oxide can be attributed to the hydrofluoric acid added to the CAA solution. Recall that the difference between the CAA method used to produce the capacitive oxide discussed in section C, and this oxide, which is neither capacitive nor inductive, was the addition of HF to the CAA solution in the latter case.

The anodic oxide produced by the CAA/HF procedure has inorganic and organic fluorine in the oxide surface ( $\leq 100 \text{ \AA}$ ) as described previously in the 1984 report<sup>(1)</sup>. The fluorine compounds would be expected to be distributed throughout the oxide and not just in the surface, however. It is generally accepted that when HF is added to the CAA solution, the oxide is built up from the metal substrate as the HF etches the metal substrate. Oxides produced by CAA with HF are more porous than oxides produced without HF<sup>(4)</sup>, presumably because the fluorine tunnels up through the oxide during formation.

TABLE XV

TEST APPARATUS MEASUREMENTS AND MEASUREMENTS FOR  
TWO PARALLEL PLATES IN SERIES WITH THE CAA/HF  
OXIDE BETWEEN THE PLATES

<u>Frequency</u>	<u>Test Apparatus (Henries)</u>	<u>Test Apparatus and Sample (Henries)</u>
120 Hz	0	0
	0	0
	0	0
	0	0
1 KHz	$300.00 \times 10^{-9}$	$300.00 \times 10^{-9}$
	$300.00 \times 10^{-9}$	$300.00 \times 10^{-9}$
	$300.00 \times 10^{-9}$	$300.00 \times 10^{-9}$
	$300.00 \times 10^{-9}$	$300.00 \times 10^{-9}$
1 MHz	$254.00 \times 10^{-9}$	$229.00 \times 10^{-9}$
	$208.00 \times 10^{-9}$	$197.00 \times 10^{-9}$
	$208.00 \times 10^{-9}$	$204.00 \times 10^{-9}$
	$208.00 \times 10^{-9}$	$176.00 \times 10^{-9}$

NOTES: (1) Oxide was electrodeposited onto Ti-6Al-4V by CAA method #1 described in Table VIII.

(2) Each test apparatus measurement was for a specific pair of probes. Each test apparatus datum in Column 2 corresponds specifically to the adjacent datum in Column 3.

This oxide composition suggests that the CAA/HF oxide would behave like a conductor rather than an inductor or capacitor. This is substantiated by the bulk resistivity data to be discussed below.

ii. Dielectric Constant of Oxide Produced by CAA with HF

Since the CAA/HF oxide was not capacitive, no determination of the dielectric constant was made.

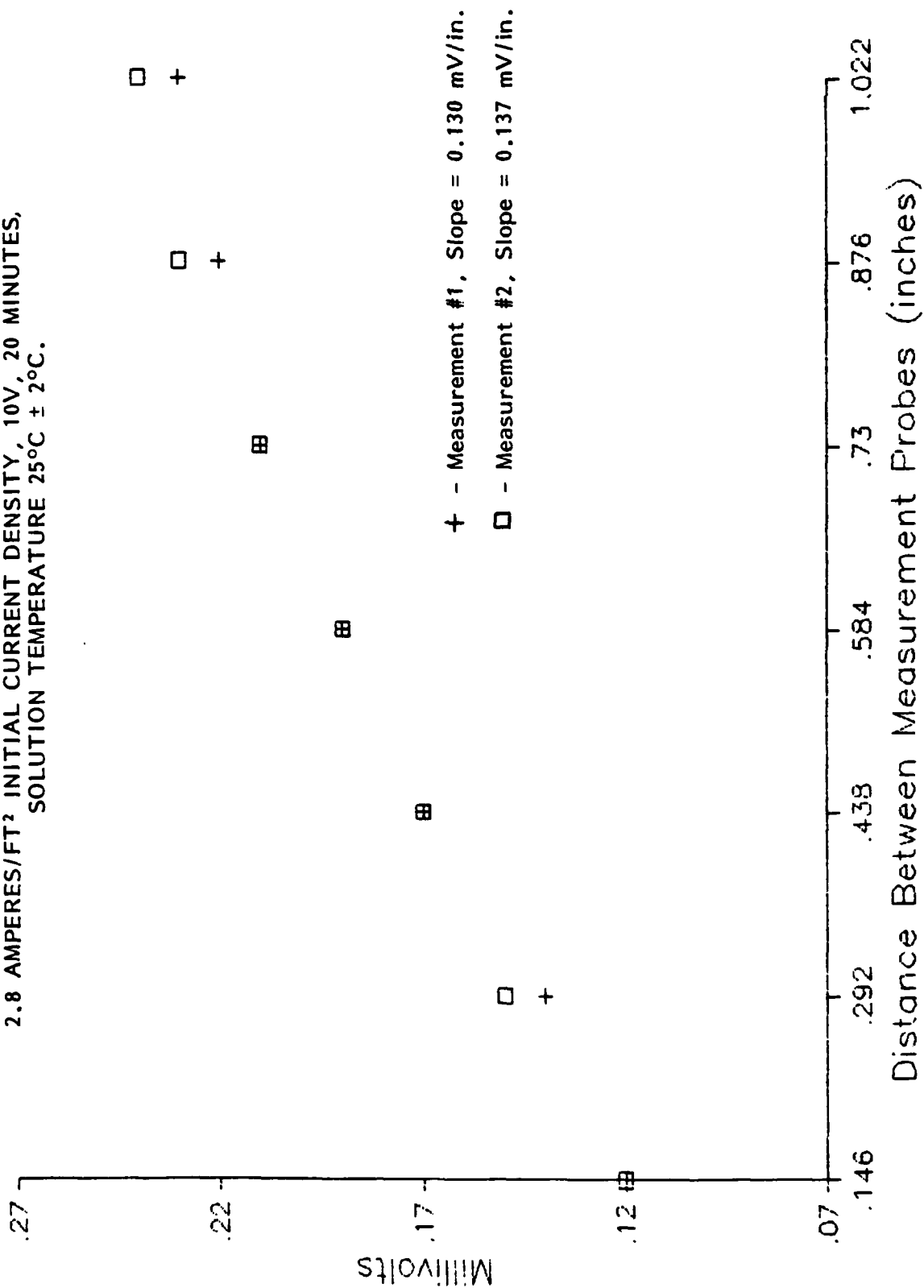
iii. Bulk Resistivity of Oxide Produced by CAA with HF

Figure 6 is the voltage vs. distance data obtained when a known potential and current were applied to the end test probes. Two sets of measurements were made. These measurements were obtained in a dry nitrogen environment at  $25^{\circ}\text{C} \pm 2^{\circ}\text{C}$ . There was a linear relationship between potential and distance. This indicates that there was no contact resistance which could interfere with any of the electrical property measurements.

The oxide bulk resistivity in dry nitrogen at  $25^{\circ}\text{C} \pm 2^{\circ}\text{C}$  was calculated based upon the average of the slope data in Figure 6, the oxide cross sectional area, and an oxide thickness of  $5.5 \mu\text{in.}$  (140 nm), based upon interferometric measurements.

The oxide bulk resistivity was calculated to be  $1.2 \times 10^{-2} \mu\Omega\text{-cm}$ . For comparative purposes, the bulk resistivity of graphite is approximately  $1.0 \times 10^{-3} \mu\Omega\text{-cm}$  and the bulk resistivity of titanium carbide is approximately  $50 \times 10^{-6} \mu\Omega\text{-cm}$ . The oxide appears to be a conductor.

Figure 6. VOLTAGE VS. DISTANCE DATA USED IN BULK RESISTIVITY DETERMINATION  
FOR CAA/HF OXIDE ON T1-6Al-4V. CAA/HF ANODIZATION PROCEDURE:  
2.8 AMPERES/FT<sup>2</sup> INITIAL CURRENT DENSITY, 10V, 20 MINUTES,  
SOLUTION TEMPERATURE 25°C ± 2°C.



#### E. Morphology and Structure of Oxide Produced on Ti-6Al-4V by CAA With HF

Transmission Electron Microscopy (TEM) and Selected Area Electron Diffraction (SAED) analyses were used to determine the morphology and structure, respectively, for an oxide produced on Ti-6Al-4V per method #5 in Table VIII.

SAED analysis of the oxide in cross section indicated that the oxide was primarily amorphous.

Figure 7 is a TEM photograph of the oxide in cross section. It can be noted that the oxide follows the metal substrate contours. The oxide roughness is approximately  $6.6 \mu\text{in.}$  (170 nm).

Figure 8 is a more magnified TEM photograph of the oxide in cross section. The regular, columnar pore structure in the oxide is evident. These columnar pores are generally considered to be beneficial to adhesive-oxide mechanical interlock.

A parallel section of the oxide is shown in Figure 9. The pore diameter was, on average,  $1.3 \mu\text{in.}$  (32 nm) with a  $0.2 \mu\text{in.}$  (6 nm) wall thickness. This is in good agreement with values reported by Cheng<sup>(4)</sup> of  $1.2 \mu\text{in.}$  (30 nm) pore diameter with a  $0.4 \mu\text{in.}$  (10 nm) wall thickness. In Cheng's work, the oxide was produced by CAA/HF of Ti-6Al-4V at 10V and a  $1.2 \text{ Ampere/ft}^2$  current density.

#### F. A Comparison of Oxide Thickness Data Obtained by Transmission Electron Microscopy and Multiple Beam Interferometry

Table VIII contains the oxide film thickness data determined both by TEM analysis of an oxide in cross section and by multiple beam interferometry (MBI). This comparison was conducted for the oxide

Figure 7. TEM PHOTOGRAPH OF CAA/HF OXIDE ON Ti-6Al-4V SUBSTRATE IN CROSS SECTION (30,000X).

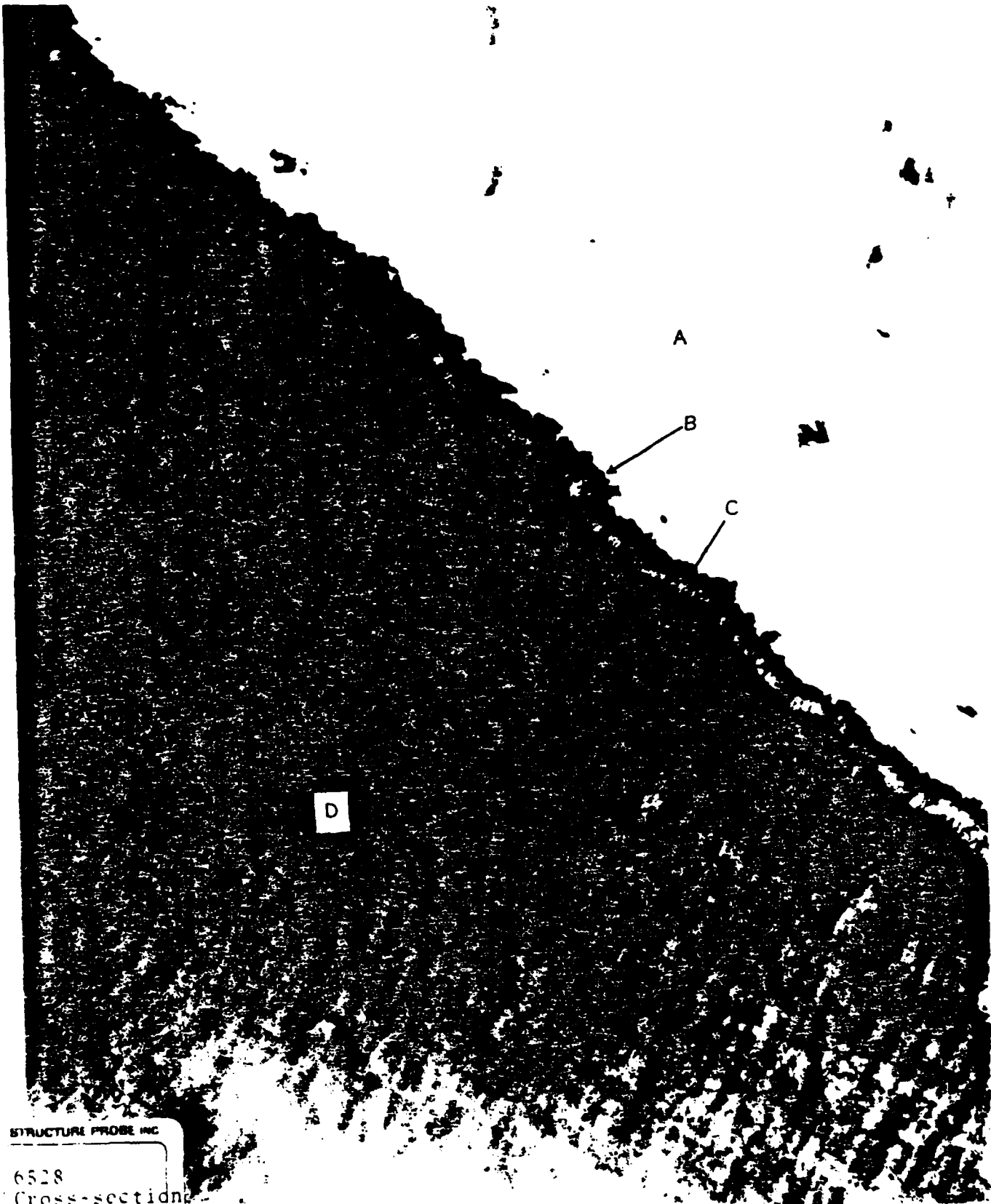
CAA/HF ANODIZATION PROCEDURE: 2.0  
AMPERES/FT<sup>2</sup> INITIAL CURRENT DENSITY, 10V,  
20 MINUTES, SOLUTION TEMPERATURE 10°C ± 2°C.

A - EPOXY MOUNT

B - GOLD DEPOSIT

C - OXIDE

D - Ti-6Al-4V SUBSTRATE



STRUCTURE PROBE INC

6528  
Cross-sectioning  
30,000X

Figure 8. TEM PHOTOGRAPH OF CAA/HF OXIDE ON Ti-6Al-4V SUBSTRATE IN CROSS SECTION (200,000X).

CAA/HF ANODIZATION PROCEDURE: 2.0 AMPERES/FT<sup>2</sup> INITIAL CURRENT DENSITY, 10V, 20 MINUTES, SOLUTION TEMPERATURE 10°C ± 2°C.

- A - EPOXY MOUNT
- B - GOLD DEPOSIT
- C - OXIDE
- D - Ti-6Al-4V SUBSTRATE



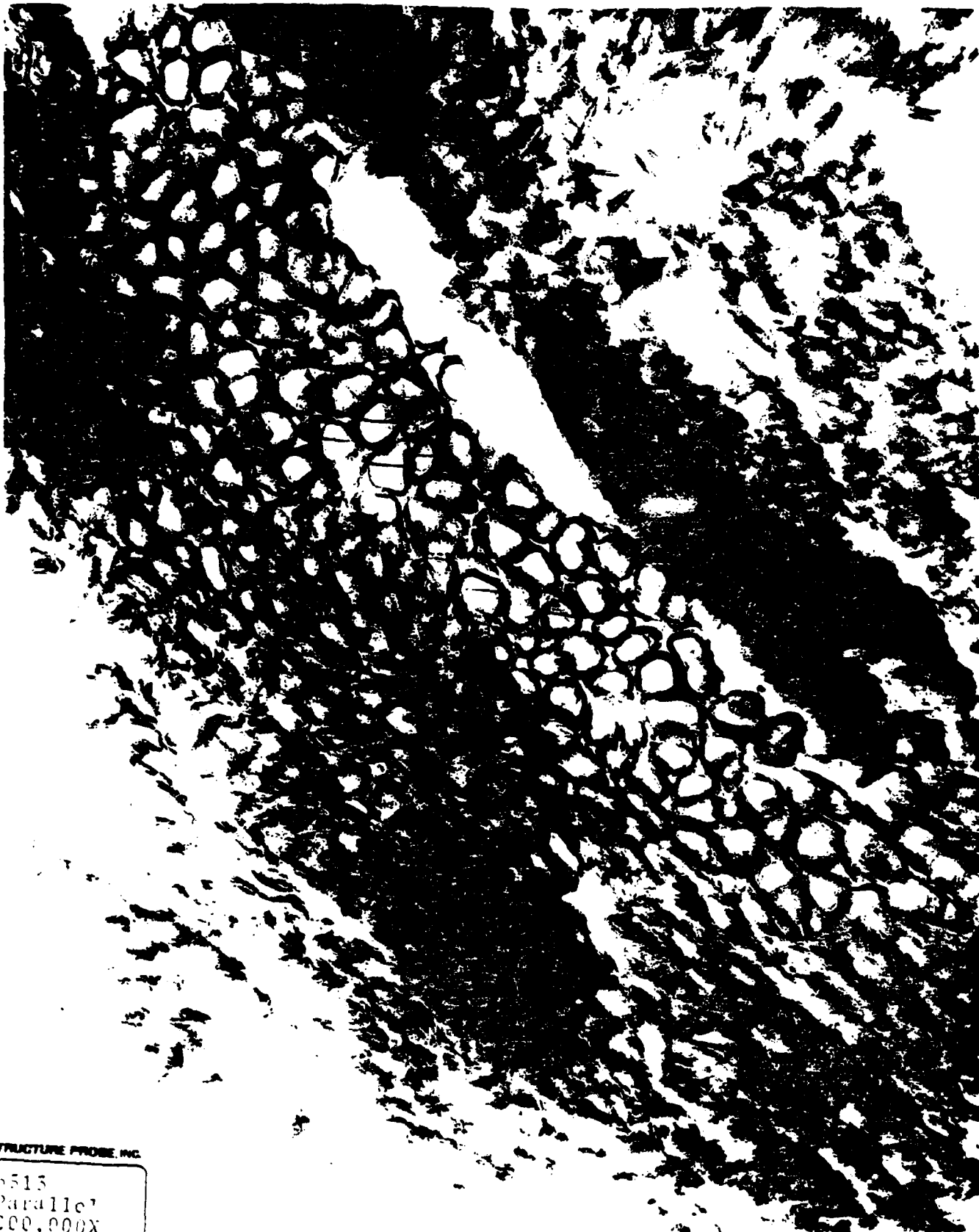
STRUCTURE PROBE, INC.

6530 E.F.  
Cross-sec#1  
200,000X

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Figure 9. TEM PHOTOGRAPH OF CAA/HF OXIDE ON Ti-6Al-4V SUBSTRATE IN PARALLEL SECTION (200,000X).

CAA/HF ANODIZATION PROCEDURE: 2.0  
AMPERES/FT<sup>2</sup> INITIAL CURRENT DENSITY, 10V,  
20 MINUTES, SOLUTION TEMPERATURE 10°C ± 2°C.



STRUCTURE PROBE, INC.

6515  
Parallo' 7  
200,000X

produced by anodization method #5, also described in Table VIII. The MBI method and data were described in the 1984 Report<sup>(1)</sup>.

It can be seen that there is good agreement between oxide thickness data obtained by these two methods. The oxide thickness per the MBI method was  $6.3 \mu\text{in.}$  (160 nm). The oxide thickness per the TEM method was  $3.7 - 5.8 \mu\text{in.}$  (95 - 150 nm). The TEM method is sensitive to oxide thickness variations whereas the MBI method is not. Because any one MBI fringe corresponds to a 0.007 in. width on the oxide substrate, this method is therefore relatively insensitive to variations in the oxide thickness.

#### IV CONCLUSIONS

- (1.) The oxide produced by CAA/HF anodization is basically amorphous and has regular columnar pores. The pore diameters were on average 1.3  $\mu$ in. (32 nm) with a 0.2  $\mu$ in. (6 nm) wall thickness.
- (2.) The CAA/HF oxide had a roughness of approximately 6.6  $\mu$ in. (170 nm).
- (3.) There was good agreement between oxide thickness measured by TEM analysis of the oxide in cross section conducted at Structure Probe, Inc., and the MBI method conducted in this lab. The advantage of the TEM technique is that it was sensitive to oxide thickness variations.
- (4.) The CAA/HF oxide was conductive. The CAA oxide was capacitive. The difference in the oxide behavior was attributed to fluorine in the oxide matrix, which caused the CAA/HF oxide to have conductive properties.
- (5.) The average dielectric constant at 1 MHz for the CAA oxide was 0.88 at  $25^{\circ}\text{C} \pm 2^{\circ}\text{C}$  in a dry nitrogen environment.
- (6.) Bulk resistivity of the CAA/HF oxide was  $1.2 \times 10^{-2} \mu\Omega\text{-cm}$  at  $25^{\circ}\text{C} \pm 2^{\circ}\text{C}$  in a dry nitrogen environment.
- (7.) The highest PPQ - anodized Ti-6Al-4V average single lap bond strength obtained in this study was  $5500 \pm 770$  psi. The average value was based on six unaged bonds. The failure mode was primarily in the adhesive, based upon visual analysis. An isothermal bonding process was used.

- (8.) The worst PPQ - anodized Ti-6Al-4V average single lap bond strength obtained in this study was  $2630 \pm 200$  psi. The average value was based on four unaged bonds. The failure mode was primarily separation of the anodic oxide from the Ti-6Al-4V substrate, based upon visual analysis. The low bond strength and failure mode were attributed to the high isochronal process temperature and pressure used in bond formation.

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